Magnetic and electrochemical investigations on anions derived from oligoketones containing fluorenone and benzophenone units. An approach to the design of stable multiradical organic materials

Andreas Behrendt,[a] Constantinos G. Screttas,*,[a] Donald Bethell,*,[b] Olav Schiemann[c] and Barry R. Steele[a]

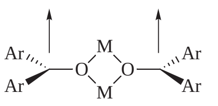
[a] *Institute of Organic and Pharmaceutical Chemistry, National Hellenic Research Foundation, 116 35 Athens, Greece*
[b] *The Robert Robinson Laboratories, University of Liverpool, PO Box 147, Liverpool, UK L69 3BX*
[c] *Fachbereich Chemie der Phillips-Universität, D-35032 Marburg, Germany*

The mono- and poly-anions of some mono-, di- and tetra-ketones containing fluorenone and benzophenone moieties have been studied by NMR and cyclic voltammetry. Alkali metal anion radicals of fluorenone, generated by electron transfer from an alkali metal naphthalene radical anion exhibit markedly lower molar paramagnetic solvent shifts than those generated by direct reduction with an alkali metal. Evidence is provided for the involvement of hyperfine interactions between the naphthalene and the paramagnetic solute. The dianion of the diketone 9 is paramagnetic as are the dianions of the tetraketones 6 and 7. The NMR data, combined with those obtained by cyclic voltammetry, indicate that polyketones possessing fluorenone moieties connected through isophthaloyl 'spacers' are promising systems for the preparation of high-spin organics and electrophores.

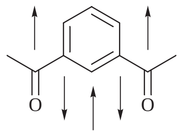
Introduction

Organic high-spin molecules are basic materials for the design of organic ferromagnets.[1] Unfortunately, most of the known stable high-spin molecules are not suitable for obtaining organic based ferromagnetic materials due to antiferromagnetic intermolecular interactions which compensate the intramolecular spin alignment in the bulk material. A promising category of compounds for the development of macroscopic high-spin systems is the class of aromatic ketone radical anions of type **A**, since both intra- and inter-molecular high-spin coupling seems possible. Recent reports[2] by Hou *et al.* have confirmed earlier conclusions arrived at by Hirota and Weissman[3] on the basis of UV and EPR data that alkali metal aromatic ketone radical anions form strongly coupled biradicals in which the metal acts as a spin-carrying centre.

It is well established that intramolecular high-spin systems can be designed by the incorporation of 1,3-aroylbenzene moieties[4] into a structure with extended conjugation of type **B**.

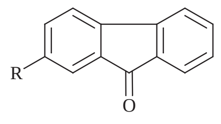


A

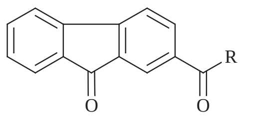


B

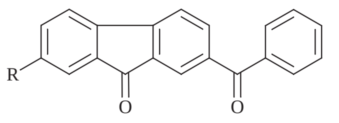
Species which fulfil both of the above described conditions could provide an approach to the design of macroscopic high-spin organic materials. Accordingly, we have synthesized and investigated the ketones **1**–**10**, most of which possess oxo-fluoren-2(7)-yl and/or benzoyl moieties. The combination of the fluorenone and benzophenone entities within a molecule seemed attractive due to their well known tendency to form stable radical anions reversibly.



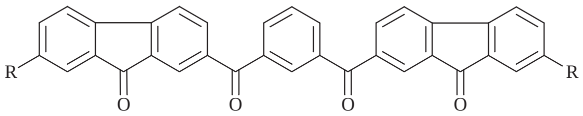
1 R = H
2 R = n–$C_{11}H_{23}$



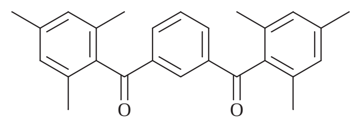
3 R = n–$C_{10}H_{21}$



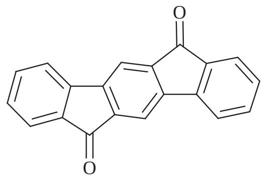
4 R = H
5 R = n–$C_{11}H_{23}$



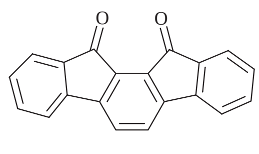
6 R = H
7 R = n–$C_{11}H_{23}$



8



9



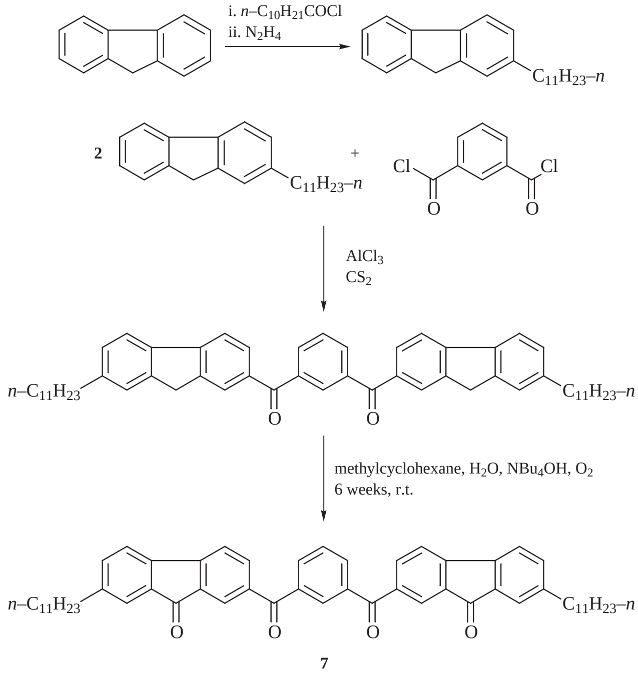
10

Matters such as (a) kinetic and thermodynamic stabilities, (b) magnetic state of mono- and poly-anions, (c) redox properties, (d) electron delocalization in the neutral and the reduced species, (e) intramolecular interactions between the subunits, (f) effect of substitution and (g) effect of added ligands, represent some important, as well as useful, pieces of information for compounds **1**–**10**. The aim of the present work is to report on these properties and, within this class of compounds, to determine the structural features necessary for the development of high-spin organic materials and electrophores.[5]

Results and discussion

(a) Syntheses and methods

The synthesis of the ketones starts from fluorene, which can be readily substituted in the 2-(7-) position(s) by Friedel–Crafts acylation giving access to alkanoyl- and benzoyl-substituted fluorenes. Oxidation of these intermediates leads to the desired oligoketones containing the fluoren-9-one moiety. For example, the tetraketone **7** was prepared *via* two-phase, base-catalysed air-oxidation of 1,3-bis(7-*n*-undecylfluoren-2-ylcarbonyl)benzene (see Scheme 1). It should be noted, however, that oxidation was extremely slow—six weeks of stirring at room temperature were necessary for complete oxidation. The low solubility of compounds **4**, **6**, **9** and **10** precluded the investigation of their mono- and di-anions at high concentrations, and we therefore undertook the synthesis of their n-$C_{11}H_{23}$-alkylated counterparts **5** and **7**. The latter compounds are soluble in solvents such as dichloromethane, chloroform or THF. Mono- and poly-anions also exhibit sufficient solubility in THF to allow measurement of their magnetic behaviour by the NMR method.[6] Two methods were used for generating mono- or poly-anions of aromatic ketones: by direct reduction with *n* equivalents of an alkali metal or by indirect reduction with *n* equivalents of a standard solution of an alkali metal aromatic hydrocarbon radical anion, *e.g.*, an alkali metal naphthalene radical anion, eqns. (1) and (2).



Scheme 1

$$\text{Ketone} + n\mathrm{M} \longrightarrow [\text{Ketone}]^{n-},n\mathrm{M}^+ \ (\mathrm{M} = \text{alkali metal}) \quad (1)$$

$$\text{Ketone} + n\mathrm{C_{10}H_8}^{\bullet-}\mathrm{M}^+ \longrightarrow [\text{Ketone}]^{n-},n\mathrm{M}^+ + n\mathrm{C_{10}H_8} \quad (2)$$

The direct method is a heterogeneous, and therefore slow, reaction, whereas the electron transfer method is a homogeneous reaction which proceeds instantaneously due to the much greater electron affinity of the ketone compared with naphthalene. An important advantage of the electron transfer method is that, by using standardized solutions of alkali metal naphthalene radical anions, one can accurately control the stoichiometry in the generation of mono- or poly-anions of oligoketones.

Table 1 Molar paramagnetic solvent NMR shifts, δ_M/ppm mol^{-1}, of the radical monoanions of compounds **1**, **2**, **5** and **7** referred to the α-proton resonance of THF at 300 K

	$[\mathrm{M}^+][\mathbf{1}^{\bullet-}]$[a]	$[\mathrm{M}^+][\mathbf{1}^{\bullet-}]$[b]	$[\mathrm{M}^+][\mathbf{2}^{\bullet-}]$	$[\mathrm{M}^+][\mathbf{5}^{\bullet-}]$	$[\mathrm{M}^+][\mathbf{7}^{\bullet-}]$[c]
Li	3.85	3.66	3.55	3.34	3.35
Na	5.60	4.55	4.19	3.92	3.95
K	6.18	5.00	4.68	4.17	4.14

[a] Fluorenone radical anion produced *via* reduction by alkali metals. [b] Fluorenone radical anion produced *via* reduction by alkali metal naphthalene radical monoanions. [c] Molar paramagnetic solvent shift derived from a 0.1 M solution.

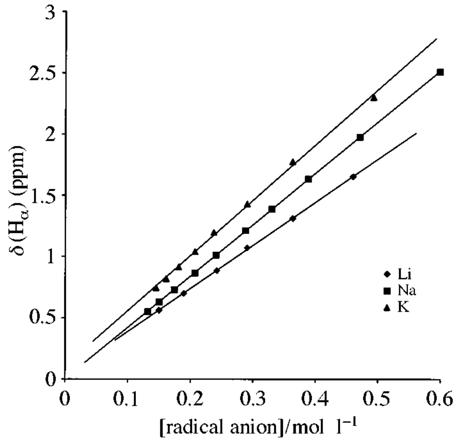


Fig. 1 Relationship between the paramagnetic solvent NMR shift for H_α of THF and the concentration of the lithium, sodium and potassium 2-*n*-undecylfluorenone radical anions

The magnetic state of the anions, $[\text{Ketone}]^{n-}$, can be examined by paramagnetic solvent NMR shift measurements.[6] Based on the linearity between the formal concentration of the paramagnetic solute and the corresponding paramagnetic solvent NMR shifts, magnetic measurements on radical anion solutions of concentrations up to 1 M are feasible. The observed shifts are composed of bulk and hyperfine contributions.[7]

(b) Paramagnetic solvent NMR shift measurements

The monoanions of the ketones **1** and **2** and **4**–**10** were generated by the electron transfer method and their molar paramagnetic solvent NMR shifts were measured, with the exception of **8**, which gave a diamagnetic solution, and **9** and **10**, which exhibit a very low solubility in THF. Table 1 summarizes the relevant data. It may be of interest to note the effect of the introduction of an alkyl group in the 2-position of fluorenone with respect to the paramagnetic solvent NMR shift of the corresponding monoanions. In Fig. 1 are given the relationships between the observed paramagnetic solvent shift and concentration for the lithium, sodium and potassium 2-*n*-undecylfluorenone radical anions. It is noted that the usual linearity between δ_{obs} and the formal concentration holds.[6] Thus, if there are oligomer or ion-pair equilibria, these do not have any corresponding effect on the dilution curves. In addition, the molar shifts, δ_M, increase from lithium to sodium to potassium, column 3, Table 1, as do the corresponding parameters for the unsubstituted fluorenone radical anions, compare columns 2 and 3. However, the molar shifts of the substituted fluorenone radical anions are considerably smaller. The same trend is also observed in the case of lithium, sodium and potassium 2-benzoyl-7-*n*-undecylfluorenone radical anions, Fig. 2, and column 4, Table 1. A smaller molar paramagnetic solvent shift could mean either that the contributing contact shift is more negative in the one case, or that there is some spin pairing which results in diminished bulk paramagnetism. The question then

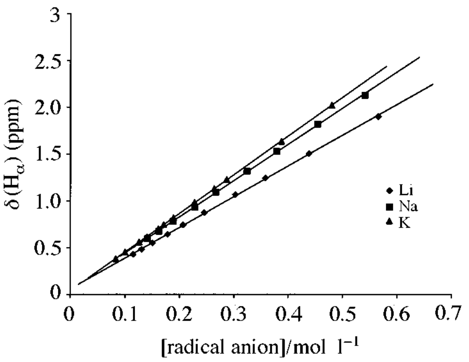


Fig. 2 Relationship between the paramagnetic solvent NMR shift for H_α of THF and the concentration of the lithium, sodium and potassium 2-benzoyl-7-*n*-undecylfluorenone radical anions

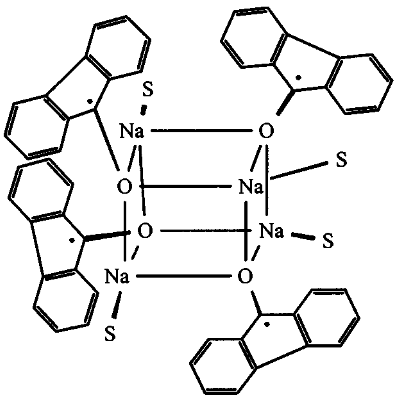


Fig. 3 Postulated structure for solvated lithium fluorenone radical anion (*cf.* ref. 2)

arises as to why a long alkyl substituent in the 2-position of fluorenone, **2**, or the 7-position in the 2-benzoylfluorenone, **5**, should cause such an effect. The existing data on the stability of radical anions[8] indicate that there is a dramatic substituent effect for this phenomenon; destabilization increases rapidly on going from methyl to ethyl, isopropyl, *tert*-butyl. We estimate[9] that the *n*-$C_{11}H_{23}$ group could exhibit a destabilizing effect almost equal to that of a *tert*-butyl group. Bearing in mind that alkali metal aromatic ketone radical anions exist in the form of oligomers both in solution[10] and in the solid state[2], it seems reasonable to assume that destabilization results in a 'tighter' aggregate or an increased degree of association of the radical anionic species. In such a 'tight' cluster (Fig. 3), some spin pairing could also be probable, resulting in a decreased paramagnetism of the solution.

The molar paramagnetic solvent NMR shifts of the monoanions of **5** and **7** differ very little. Given that both compounds exhibit almost identical structural features, it is tempting to attribute this near coincidence in the corresponding δ_M values to the localization of the unpaired electron in one of the oxofluorenyl moieties. If this assumption were valid, one should expect the dianion $\mathbf{7}^{2-}$ to be paramagnetic, simply because the second electron would rather occupy the unreduced oxofluorenyl moiety. This situation was found to be the case (see following paragraph).

(c) Di- and poly-anions

The dianions of the diketones **3**–**5**, **8**, **9** and the tetraketones **6** and **7** were generated by electron transfer from two equivalents of an alkali metal naphthalene radical anion. All diketones, with the exception of **9**, gave solutions of dianions which were diamagnetic. Thus it appears that, of the diketones, only **9** possesses a doubly degenerate LUMO. The tetraketones **6** and **7** gave solutions of dianions which exhibited a paramagnetic solvent NMR shift double the value of the monoanions. The

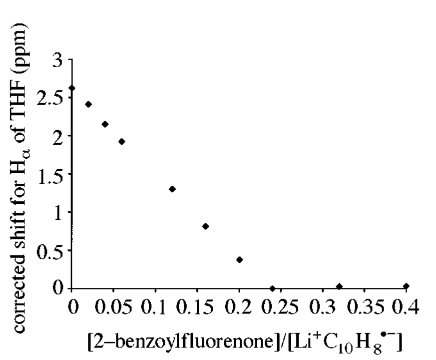


Fig. 4 Magnetic titration of lithium naphthalene radical anion against 2-benzoylfluorenone in THF

molecular symmetry of the tetraketones results in a doubly degenerate LUMO, with both levels singly occupied in the dianion. Simple (extended Hückel) calculations on the ketones studied have been made but must be treated with caution. While they do indeed indicate a nearly degenerate LUMO for the tetraketones **6** and **7**, with LUMO–NLUMO gaps of 0.005 and 0.004 eV respectively, they also indicate that the dianion from **8** should probably be paramagnetic (LUMO–NLUMO gap 0.233 eV) and that from **9** should be diamagnetic (LUMO–NLUMO gap 1.01 eV), *i.e.*, opposite to that observed. Clearly the structure of the dianions in solution requires a more sophisticated treatment. Preliminary studies on the dianion of **8** which take into consideration the counterion and the solvent suggest that the electronic configuration is very sensitive to the geometry of the system. Such calculations thus have limited value at this stage.

In order to determine the highest number of electrons that can be accommodated by a diketone, *e.g.* **4**, we carried out a magnetic titration of lithium naphthalene radical anion against the diketone. The results given in Fig. 4 indicate that there is a well-defined equivalence point at a ratio of $[Li^+C_{10}H_8^{\bullet-}]/[\mathbf{4}] = 0.25$, *i.e.*, the diketone can be reduced down to the tetra-anion. Generating tri- and tetra-anions of the diketones **3**–**5** and **8**, by three or four equivalents of an alkali metal naphthalene radical anions produced solutions which were diamagnetic. This clearly indicates that there is no stable trianion formed which otherwise should be paramagnetic. The lack of paramagnetism in trianions could be due to one of several possible reactions: dimerization, disproportionation or solvent cleavage. By adding three equivalents of an alkali metal naphthalene radical anion to a solution of **7**, we obtained paramagnetic solutions. These solutions exhibited a smaller molar shift than the corresponding dianions.

(d) Naphthalene as a ligand

Having generated the monoanions of the ketones **2** and **5** by electron transfer from the appropriate alkali metal naphthalene radical anion, we decided to compare the results obtained for a given monoanion generated by the two alternative methods of reduction. Using fluorenone itself (FlO), we measured the molar paramagnetic solvent shift for a solution of $FlO^{\bullet-}Na^+$ prepared by direct reduction with sodium metal and we confirmed the reported[6,11] molar paramagnetic solvent shift. A solution of $FlO^{\bullet-}Na^+$ was then prepared by reducing fluorenone with one equivalent of sodium metal in the presence of one equivalent of naphthalene. The relationships between the solvent shift and concentration are given in Fig. 5. We notice that the two straight lines do not coincide and that the straight line corresponding to the solution containing naphthalene exhibits a considerably smaller slope. It should be stressed that the aromatic solvent induced shift, ASIS, contribution of naphthalene to the observed shift is very small, and therefore the effect of naphthalene on the structure of sodium fluorenone radical anion in solution is real and significant. Analogous

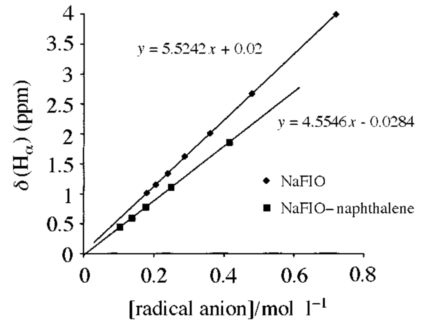


Fig. 5 Relationship between paramagnetic solvent NMR shift for H_α of THF and the concentration of sodium fluorenone radical anion ($FlO^{\bullet -}$) generated by direct reduction and by electron transfer from sodium naphthalene radical anion

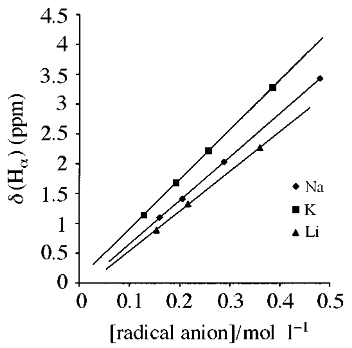


Fig. 6 Paramagnetic NMR shift of α-carbons in naphthalene induced by lithium, sodium and potassium fluorenone radical anion as a function of the concentration

Table 2 Molar paramagnetic solvent NMR shifts, δ_M/ppm mol^{-1} induced to the C-13 resonances of naphthalene by alkali metal fluorenone radical anions, $[M^+][FlO^{\bullet -}]$, in THF at 300 K

Naphthalene carbon	$[Li^+][FlO^{\bullet -}]$	$[Na^+][FlO^{\bullet -}]$	$[K^+][FlO^{\bullet -}]$
δ_{obs}(C-1)	6.55	7.23	8.41
δ_{obs}(C-9)	4.62	5.23	5.68
δ_{obs}(C-1)/δ_{obs}(C-9)	1.42	1.38	1.44

behaviour is exhibited by lithium and potassium fluorenone radical anions, compare columns 1 and 2, Table 1. This prompted us to investigate the interaction between $FlO^{\bullet -}M^+$ (M = Li, Na, K) and naphthalene. We reasoned, that, if such an interaction were operable, we should be able to observe hyperfine interactions between the paramagnetic solute and naphthalene. We chose to measure ^{13}C shifts of naphthalene resonances, induced by $FlO^{\bullet -}M^+$. In Fig. 6 the shift of the α-carbon is plotted *versus* the concentration of the radical anion, and Table 2 summarizes the observed molar shifts for the C-1 and C-9(10) resonances of naphthalene as well as the ratios of the two molar shifts referred to the two types of carbons. We notice that the two types of resonance undergo markedly different shifts and that there is a marked dependency of the molar shifts for both carbons on the cation which follows the usual trend, *i.e.*, increasing slope from Li to Na to K. In addition, the observed molar shifts referred to C-1 are markedly greater than the susceptibility shift, 5.23 ppm mol^{-1}. Therefore, not only does naphthalene experience the susceptibility shift, but the observed shift includes also hyperfine contributions. Another piece of evidence corroborating the involvement of contact interactions is the effect of chromium acetylacetonate on the naphthalene C-13 resonances. The three unpaired spins of $Cr(acac)_3$ shift the two types of C-13 resonances of naphthalene by an amount close to the theoretical susceptibility only shift, *i.e.* 26.16 ppm mol^{-1} at 300 K[12] (namely, 28.32 and 26.42 ppm mol^{-1}, for C-1 and C-9, respectively). The ratio of the two molar shifts is equal to 1.07, *i.e.* a value which differs markedly from those listed in Table 2. Obviously, chromium acetylacetonate induces almost exclusively susceptibility shifts to the C-13 resonances of naphthalene. In $Cr(acac)_3$ the acetylacetonate chelate ligands are rigidly coordinated to the low-spin substitutionally inert d^6 metal centre, which makes the transfer of spin density from the chromium cation to the magnetic nuclei of naphthalene impossible.

On the basis of electron affinities, it appears almost certain that in the $FlO^{\bullet -}M^+$ naphthalene system there should be no naphthalene radical anion. Thus the observed shifts of the C-13 resonances of naphthalene apparently include contributions arising from hyperfine interactions between the fluorenone radical anion and naphthalene. Compounds which can develop covalencies[13] with alkali metal cations can receive spin density from the ketone radical anion to which the alkali metal is covalently bonded *via* multicentre bonds in the oligomer. It is possible, therefore, that the naphthalene, by virtue of its π-basicity,[14] may be π-bonded to the cation, making possible the transfer of spin density to the magnetic nuclei of naphthalene. Another possible mechanism is a through-space interaction which requires the involvement of dipolar interactions. However, this alternative seems to be less probable due to the expected labile character of the π-complex and the rapid exchange between free and complexed naphthalene, a situation which should cause dipolar contributions to average to zero. The effect of naphthalene upon the structure of alkali metal fluorenone radical anions is further manifested by the observed diminishing cation dependency of the molar paramagnetic solvent NMR shift. This can be seen by comparing the relative molar paramagnetic solvent NMR shifts δ_M (Li) : δ_M (Na) : δ_M (K) in the absence and the presence of naphthalene. The corresponding ratios are 1 : 1.44 : 1.60 and 1 : 1.24 : 1.37, which imply a preference of naphthalene for the larger cations.

(e) Electrochemistry

Since the anions were generated in THF we used the same solvent for the cyclic voltammetry measurements. The electrochemical data of the ketones **1**, **2**, **3**, **4**, **5**, **7** and **8** are listed in Table 3.

With the exception of **8**, the first reduction process to the monoanion of the above ketones occurs reversibly. As expected for fast electron transfer reactions, peak to peak separations are 57 mV and the ratio between cathodic and anodic peak current is unity. The first reduction process should take place at the fluorenone moiety, a conclusion arrived at by comparison of the redox potentials of fluorenone and the investigated ketones. This assumption is also in agreement with EPR spectroscopic studies on derivatives of fluorenone.[15] Alkyl substituents on the fluorenone moiety cause a slight increase in the electron density on the aromatic system (+I-effect) and the transfer of an additional electron becomes more difficult. Thus the reduction potentials of **2** and **5** are 15 mV more negative in comparison to **1** and **4**, respectively. In contrast to alkyl substitution, introduction of an R–CO group to the fluorenone moiety, shifts the reduction potential in the anodic direction substantially—in our cases by 140 mV for R = n-$C_{10}H_{21}$ and 160 mV for R = Ph. In the latter cases, electron density is removed from the fluorenone moiety so the LUMO can readily accept a second electron. For the tetraketone **7**, the first reduction apparently occurs as a two-electron transfer step, most probably at the fluorenone moieties, Fig. 7. That this wave really represents a two-electron transfer step was confirmed by controlled potential electrolysis. No redox splitting between the potentials $E_{\frac{1}{2}}(7/7^-)$ and $E_{\frac{1}{2}}(7/7^{2-})$ is observed, but the peak to peak separation of the wave is increased from the ideal 57 to 78 mV.

All of the ketones investigated contain the fluorenone moiety and exhibit a reversible redox wave for the second reduction.

Table 3 Electrochemical data for compounds **1**, **2**, **3**, **4**, **5**, **7** and **8**. CV scans in THF–0.1 M NBu_4ClO_4 at platinum *versus* SCE at 298 K

	1	**2**	**3**	**4**	**5**	**7**	**8**
$E_{\frac{1}{2}}(0/-1)$/V	−1.301	−1.315	−1.160	−1.138	−1.166	−1.135[a]	−1.752
ΔE/μV	59	61	58	66	56	78	irrevers
$I_{pa/pc}$	1	1	1	1	1	1	
$E_{\frac{1}{2}}(-1/-2)$/V	−2.060	−2.075	−1.845	−1.798	−1.807	*b*	−2.348
ΔE/μV	64	77	73	65	73		irrevers
$I_{pa/pc}$	1	1	1	1	1		
$E_{\frac{1}{2}}(-2/-3)$/V			−2.738 V[c] irrevers	−2.334 V irrevers	−2.343 V irrevers	−2.343 V irrevers	
ECE[d]				−2.165 V	−1.339 V	−1.320 V	
ECE				−2.362 V	−2.772 V	−2.453 V	

[a] 2e-transfer process leading to 7^{2-}. [b] Redox splitting $E_{\frac{1}{2}}(-2/-3) = -1.758$ V; $E_{\frac{1}{2}}(-3/-4) = -1.908$ V. [c] Only observed at −35 °C. [d] Anodic peak current only observed after having previously performed the irreversible process, $E_{\frac{1}{2}}(-2/-3)$.

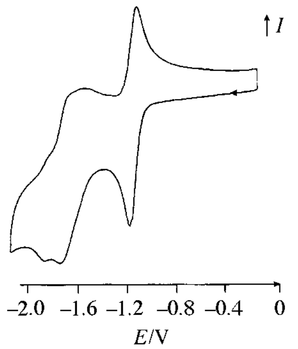


Fig. 7 CV scan of **7** in THF–0.1 M Bu_4NClO_4 at platinum, $T = 298$ K, $v = 100$ mV s^{-1}

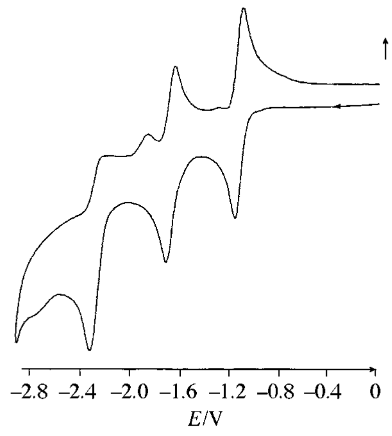


Fig. 8 CV scan of **5** in THF–0.1 M Bu_4NClO_4 at platinum, $T = 298$ K, $v = 100$ mV s^{-1}

Anodic and cathodic shifts for the process $E_{\frac{1}{2}}(-1/-2)$ of the latter compounds in comparison to the $E_{\frac{1}{2}}(-1/-2)$ of the unsubstituted fluorenone, **1**, follow trends analogous to those observed for the potentials $E_{\frac{1}{2}}(-1/-2)$. However, the relative anodic shifts of **4** and **5** for the process $E_{\frac{1}{2}}(-1/-2)$, as compared to that of **1**, are higher than the corresponding shifts for the first reduction (see Fig. 8) This behaviour is indicative of a benzophenone-like character of the HOMO in the dianions.

Whereas in the monoanions most of the electron density is located on the fluorenone moiety, an important question arises as to whether both of the additional electrons are localized on the fluorenone moiety, as in the case of the monoanion, or whether they undergo a rapid hopping between the fluorenone and the 'benzophenone' moieties leading to an effective delocalization of electron density. Since the reduction potentials $E_{\frac{1}{2}}$(fluorenone$^-$/fluorenone^{2-}) and $E_{\frac{1}{2}}$(benzophenone/benzophenone$^-$) are approximately the same, the benzoyl group could attract considerable electron density in the dianions. Also, the electron–electron repulsion of the additional two electrons would make the delocalization appear reasonable.

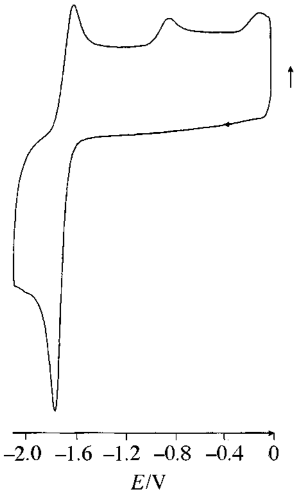


Fig. 9 CV scan of **8** in THF–0.1 M Bu_4NClO_4 at platinum, $T = 298$ K, $v = 400$ mV s^{-1}

In view of the fact that for **7** the wave at −1.135 V in the cyclic voltammogram represents a two-electron transfer step, leading directly to the stable dianion 7^{2-}, one would also expect a common wave for the reduction processes $7^{2-}/7^{3-}$ and $7^{3-}/7^{4-}$ with similar reduction potential to that of the second reduction of **5**, *i.e.* −1.8 V. However, in this potential range the cyclic voltammogram of **7** shows two reversible waves separated by 150 mV which, by comparison of the peak currents, can be interpreted as one-electron transfer steps. This redox splitting for the processes $7^{2-}/7^{3-}$ and $7^{3-}/7^{4-}$ confirms our conclusion that, in dianions of benzoyl substituted fluorenones, there is substantial electron density on the 'benzophenone' moiety. Accordingly, in 7^{3-} the third additional electron is presumed to have high electron density on the isophthaloyl moiety and, for electrostatic reasons, makes the transfer of the fourth electron more difficult, thus causing the observed redox splitting.

In the cyclic voltammograms, all diketones exhibited irreversible redox behaviour for the process DK^{2-}/DK^{3-}, even at high scan rates. The redox potentials are very close to the second irreversible reduction of benzophenone. The irreversible character is in agreement with our results from the magnetic titrations where no paramagnetic trianionic species could be detected. The occurrence of several peaks arising *via* an ECE-mechanism indicate that trianions, due to their instability, undergo one of the possible reactions, namely dimerization, reaction with solvent or reaction with the supporting electrolyte.

Table 4 UV-absorption bands, λ_{max}/nm, and extinction coefficients (in parentheses), ε/l cm^{-1} mol^{-1}, of the ketones **1**, **2**, **3**, **4**, **5** and **7** in THF at 298 K

Band	1	2	3	4	5	7
I				not resolved	248.6 (37 046)	248.9 (67 637)
II				248.5 (30 337)	254.2 (38 101)	254.4 (70 804)
III	248.4 57 777	254.0 (62 062)	not resolved	254.2 (29 572)	260.6 (33 816)	260.5 (62 634)
IV	256.9 84 760	261.1 (95 562)	271.9 (55 368)	274.9 (43 977)	280.8 (43 230)	283.0 (73 211)
V	293.5 (3809)	295.2 (5750)	298.9 (5947)			
VI	307.2 (1769)	308.2 (2199)	315.1 (2908)	315.8 (5252)	319.6 (7514)	321.4 (17 859)
VII	322.7 (847)	324.2 (544)		330.0 (2131)	333.71 (4596)	335.2 (11 526)
VIII[a]	(275)	(327)	(780)	(979)	(1117)	(2477)

[a] Broad absorption band around 380 nm whose vibrational structure is not clear.

Diketone **8** is the only compound which cannot be reversibly reduced under our experimental conditions (Fig. 9). The ratio between cathodic and anodic current for the corresponding reduction process at -1.75 V is much less than unity. Obviously $\mathbf{8}^{\bullet-}$ undergoes a very rapid reaction, which is manifested by waves in the cyclic voltammogram at -0.85 and -0.085 V, which can only be detected if the reduction is previously performed at -1.725 V. It is important to note that **8**, whose monoanion is unstable, is indeed the only compound under investigation without the fluorenone fragment. The electrochemical instability of the monoanion is in accordance with the paramagnetic NMR shift measurement (see above).

(f) UV–VIS spectroscopy

UV–VIS spectra have been recorded for compounds **1**, **2**, **3**, **4**, **5** and **7** and the results are given in Table 4. As found by Kuboyama, unsubstituted fluorenone shows UV-absorption bands at wavelengths near 380, 310, 290 and 250 nm, respectively.[16] They can all be attributed to π–π* transitions. Unfortunately, the structure of the 380 nm band is not clear. The comparison between the ketones under investigation demonstrates that the absorption bands of the different transitions are slightly shifted to higher wavelengths in the case of the substituted fluorenones. The shift is to longer wavelengths in all cases, regardless of the electron-donating or electron-withdrawing properties of the substituents. Furthermore, we notice that benzoyl and alkanoyl substituents lead to a significant decrease in the extinction coefficients in the region of absorption bands >300 nm. The extinction coefficients of the diketones **3**, **4**, **5** and **7** in this region are higher than those of fluorenone, **1**, and the alkylated fluorenone **2**. It is perhaps worth mentioning that the absorption bands of the tetraketone **7** have approximately double the intensity of those of **5**, which is reasonable if we consider that **7** is composed of two units of **5**.

Since we have shown that the electron-donating alkyl substituent shifts the reduction potentials $E_{\frac{1}{2}}(0/-1)$ and $E_{\frac{1}{2}}(-1/-2)$ in the cathodic direction while the electron-withdrawing acyl substituents facilitate the reduction, the question then arises why both types of substituent can cause a shift of the transition bands in the UV spectra to higher wavelengths. However, we must bear in mind that on reduction the additional electron enters the LUMO, whereas it is the gap between occupied and unoccupied orbitals which determines the locations of the transitions bands. This gap may be affected differently by the alkyl and acyl substituents. Since we could not detect any oxidation process in the potential range up to two volts, we have no electrochemical information about the relative location of the HOMOs, and therefore it is not possible to correlate electrochemical potentials with the results derived from UV-spectroscopy.

Conclusions

The benzoyl-substituted fluorenones formed stable monoanions on reduction with one equivalent of an alkali metal naphthalene radical anion. All experimental data point to the conclusion that the unpaired electron resides on the fluorenone moiety. The diketones **3**–**5** form diamagnetic solutions of stable dianions, whereas diketone **9** forms a paramagnetic dianion. The tetraketones **6** and **7**, as well as forming stable monoanions, also form stable paramagnetic dianions in solution. Hence the dianions of **6** and **7** may be regarded as biradicals, in which each fluorenone moiety carries one unpaired electron. Therefore, polyketones bearing fluorenone units bonded through an isophthaloyl spacer, should give access to stable multiradical species with potential uses as high-spin organic materials or electrophores.

Experimental

General

Magnetic titrations were carried out with a Bruker AC-300 NMR spectrometer. The same instrument was used for recording NMR spectra. Ketones **9** and **10** were synthesized according to the literature.[17] Alkali metal naphthalene radical anions were prepared in 20 mmol quantities and in concentrations of 0.5 or 1 mol l^{-1} under an atmosphere of argon by stirring equivalent amounts of naphthalene and the alkali metal in THF. The solvent was doubly distilled from fluoren-9-ylpotassium shortly before use. The concentration of the radical anion was determined by hydrolysing an aliquot of the ketyl anion solution and titrating for total alkalinity. The standardized solution of naphthalene radical anion was used for generating the radical anions and the polyanions of the ketones by mixing with the appropriate volume of a standard solution of the latter. Standard solutions were handled with microsyringes.

The solvent ^{1}H NMR shifts referred to the low field THF proton signal were recorded, and the relationship between observed shift and concentration of the paramagnetic species was constructed by recording the solvent resonance after each dilution. Electrochemical measurements were carried out at room temperature in tetrahydrofuran containing 0.1 mol dm^{-3} NBu_4ClO_4. A PC-controlled EG&G-PAR 273 instrument was used as potentiostat. A conventional 3-electrode cell was used, with Pt working and counter electrodes, and an SCE reference. UV-spectra were recorded in THF on a Perkin Elmer Lambda 2 instrument.

Syntheses

(a) 2-Undecylfluorenone, 2. (i) Fluorene (20 g, 0.12 mol) and $AlCl_3$ (18 g, 0.13 mol) were dissolved in CS_2 (80 cm^3). After addition of undecanoyl chloride (22 g, *ca.* 0.11 mol), the mixture was stirred overnight at room temperature. The solvent was evaporated and the residue hydrolysed in water–HCl (500 cm^3). The crude product was collected on a Buchner funnel and washed several times with 100 cm^3 portions of water. Several recrystallizations from isopropanol afforded white crystals (27.0 g, 68%) of 2-undecanoylfluorene δ_C(75 MHz; CDCl$_3$; Me$_4$Si) 200.3 (C=O), 146.1, 144.4, 143.2, 135.5, 127.8, 127.3, 126.9, 125.1, 124.6, 120.7, 119.5 (aromatic), 38.7, 36.8, 31.8, 29.6–29.2, 24.5, 22.6, 14.0 (aliphatic), which was used without further purification for the following stage.

(ii) Sodium (10 g) was dissolved in diethylene glycol (250 cm^3) with stirring at room temperature. 2-Undecanoylfluorene (15 g, 0.045 mol) and hydrazine hydrate (22 cm^3) were added in portions and the mixture refluxed for 15 h. After cooling the mixture was poured into cold water (100 cm^3). The precipitate was filtered, washed several times with large amounts of water and recrystallized from isopropanol. Yield of 2-undecylfluorene: 8.9 g, 62%, δ_C(75 MHz; CDCl$_3$; Me$_4$Si) 143.4, 143.1, 141.8, 141.7, 139.3, 126.9, 126.6, 125.0, 124.9, 119.5 (aromatic), 36.8, 36.2, 29.6–29.3, 22.7, 14.1 (aliphatic), which was used without further purification for the following stage.

(iii) 2-Undecylfluorene (10 g) was suspended in a mixture of methylcyclohexane (300 cm^3) and water (40 cm^3). *n*-Bu$_4$NBr (5 g) and KOH (20 g) were added and the mixture stirred for several days. The progress of the reaction was monitored by thin layer chromatography. When the conversion to the ketone was complete, the organic phase was separated from the water, washed several times with dilute hydrochloric acid and water and then evaporated. Recrystallization from isopropanol afforded 2-undecylfluorenone as yellow needles (8.4 g, 80%), mp 48 °C (Found: C, 86.0; H, 8.9. Calc. for C$_{24}$H$_{30}$O: C, 86.2; H, 9.0%). δ_C(75 MHz; CDCl$_3$; Me$_4$Si) 194.1 (C=O), 144.6, 144.4, 141.9, 135.5, 134.2, 128.5, 127.8, 125.2, 124.2, 120.7, 120.0, 119.9 (aromatic), 35.8, 31.8, 29.5–29.1 (m), 22.6, 14.1 (aliphatic); *m*/*z* (EI–MS) 334 (M$^+$, 40%), 193 (100).

(b) 2-Undecanoylfluorenone, 3. Air oxidation of 2-undecanoylfluorene by a procedure analogous to that for 2-undecylfluorene yielded **3** (85%), mp 115 °C (Found: C, 82.7; H, 8.0. Calc. for C$_{24}$H$_{28}$O$_2$: C, 82.7; H, 8.1%). δ_C(75 MHz; CDCl$_3$; Me$_4$Si) 198.9 (C=O), 148.2, 143.2, 137.5, 134.9, 134.8, 134.7, 134.2, 130.1, 124.5, 123.7, 121.1, 120.3 (aromatic), 38.7, 31.8, 29.5–29.2, 22.6, 14.0 (aliphatic); *m*/*z* (EI–MS) 348 (M$^+$, 5%), 222 (100), 207 (72), 151 (25).

(c) 2-Benzoyl-7-undecylfluorenone, 5. (i) 2-Benzoyl-7-undecylfluorene was obtained by Friedel–Crafts reaction of undecylfluorene with benzoyl chloride by a procedure analogous to that for 2-undecanoylfluorene (yield 72%) and used without further purification in the following step. δ_C(75 MHz; CDCl$_3$; Me$_4$Si) 196.7 (C=O), 146.2, 144.7, 143.3, 142.9, 138.2, 138.1, 135.3, 132.0, 129.9, 129.7, 128.2, 127.4, 126.7, 125.2, 120.5, 119.0 (aromatic), 36.7, 36.2, 31.9, 31.7, 29.6–29.3 (m), 22.6, 14.0 (aliphatic).

(ii) Air oxidation of 2-benzoyl-7-undecylfluorene by a procedure analogous to that for 2-undecylfluorene yielded **5** (81%), mp 84–85 °C (Found: C, 84.8; H, 7.75. Calc. for C$_{30}$H$_{34}$O$_2$: 84.9; H, 7.8%). δ_C(75 MHz; CDCl$_3$; Me$_4$Si) 195.1, 192.9 (C=O), 148.2, 145.8, 140.8, 137.8, 137.2, 136.7, 135.0, 134.9, 134.0, 132.6, 129.7, 128.4, 125.7, 124.6, 121.0, 119.9 (aromatic), 35.8, 31.8, 29.6–29.3, 22.6, 14.0 (aliphatic); *m*/*z* (EI–MS) 438 (M$^+$, 100%), 297 (87), 149 (58), 105 (46), 71 (32), 57 (40).

(d) Tetraketone, 6. Fluorene (10 g, 0.06 mol) and AlCl$_3$ (20 g, 0.15 mol) were dissolved in CS$_2$ (50 cm^3). Isophthaloyl dichloride (6.1 g, 0.03 mol) was added and the mixture stirred at room temperature overnight. Working up as described for 2-undecanoylfluorene yielded 1,3-bis(fluoren-2-ylcarbonyl)benzene as a cream coloured powder (7.8 g, 56%). Air oxidation of the latter yielded **6** (mp 260–262 °C) (Found: C, 82.1; H, 4.0. Calc. for C$_{34}$H$_{18}$O$_4$: C, 83.25; H, 3.7%). NMR spectra could not be measured due to insolubility. *m*/*z* (EI–MS) 490 (M$^+$, 39%), 311 (17), 207 (100), 179 (22), 151 (47).

(e) R-TK-R, 7. 1,3-Bis(7-undecylfluoren-2-ylcarbonyl)benzene was obtained by Friedel–Crafts reaction of two equivalents of undecylfluorene with one equivalent of isophthaloyl chloride by a procedure analogous to that for 1,3-bis(fluoren-2-ylcarbonyl)benzene (yield 57%). δ_C(75 MHz; CDCl$_3$; Me$_4$Si) 195.7 (C=O), 146.6, 144.7, 143.5, 143.1, 138.5, 138.0, 134.8, 132.9, 130.8, 129.7, 128.3, 127.4, 126.7, 125.2, 120.6, 119.0 (aromatic), 36.7, 36.2, 29.6–29.3 (m), 22.6, 14.0 (aliphatic). Air oxidation by a procedure analogous to that described for undecanylfluorene yielded **7** (87%). Six weeks of stirring were necessary, purification was achieved by column chromatography (eluent: 100:1 CH$_2$Cl$_2$–ethyl acetate), mp 182–184 °C (Found: C, 83.8; H, 7.4. Calc. for C$_{56}$H$_{62}$O$_4$: C, 84.2; H, 7.8%). δ_C(75 MHz; CDCl$_3$; Me$_4$Si) 194.0, 192.7 (C=O), 148.5, 145.9, 140.7, 137.1, 136.8, 135.1, 135.0, 134.2, 133.4, 130.8, 128.9, 125.5, 124.5, 121.1, 120.0 (aromatic), 35.8, 31.9, 31.8, 31.0, 29.6–29.1, 22.6, 14.0 (aliphatic); *m*/*z* (EI–MS) 798 (M$^+$, 100%), 517 (14), 258 (21), 43 (23).

Acknowledgements

This work was supported by the Human Capital and Mobility Programme, Network Contract ERBCHRXCT930148.

References

1 J. S. Miller and A. J. Epstein, *Angew. Chemie*, 1994, **106**, 399; *Angew. Chemie Int. Ed. Engl.*, 1994, **33**, 385; M. Baumgarten and K. Müllen, *Top. Curr. Chem.*, 1994, **169**, 1.

2 Z. Hou, A. Fujita, H. Yamazaki and Y. Wakatsuki, *J. Am. Chem. Soc.*, 1996, **118**, 2503; Z. Hou, T. Miyano, H. Yamazaki and Y. Wakatsuki, *J. Am. Chem. Soc.*, 1995, **117**, 4421.

3 N. Hirota and S. I. Weissman, *Mol. Phys.*, 1962, **5**, 537; N. Hirota, *J. Am. Chem. Soc*, 1967, **89**, 32.

4 W. T. Borden and E. R. Davidson, *Acc. Chem. Res.*, 1981, **14**, 69; W. T. Borden, *Mol. Cryst. Liq. Cryst.*, 1993, **232**, 195.

5 K. Müllen, *Pure Appl. Chem.*, 1993, **65**, 89; U. Müller, M. Adam and K. Müllen, *Chem. Ber.*, 1994, **127**, 437; H. Naarmann, *Angew. Makromol. Chem.*, 1982, **109/110**, 295.

6 C. G. Screttas and M. Micha-Screttas, *J. Org. Chem.*, 1981, **46**, 993.

7 C. G. Screttas and M. Micha-Screttas, *J. Org. Chem.*, 1983, **48**, 153.

8 R. G. Lawler and C. T. Tabit *J. Am. Chem .Soc.*, 1969, **91**, 5671.

9 The ionization potentials (E_I) of normal alkyl radicals from ethyl to pentyl are connected to the respective carbon numbers n_c through the relation $E_I(n\text{-R}) = -0.169n_c + 8.679$. By extrapolation we obtain an estimate for the E_I of the *n*-C$_{11}$H$_{23}$ equal to *ca.* 6.8 eV, which is close to that of the *tert*-butyl radical, 6.7 eV. For the E_I(R)s as substituent constants see C. G. Screttas and G. A. Heropoulos, *J. Org. Chem.*, 1993, **58**, 1794 and references therein.

10 C. G. Screttas and M. Micha-Screttas, *J. Am. Chem. Soc.*, 1987, **109**, 7573.

11 The reported molar paramagnetic solvents shifts of alkali metal fluorenone radical anions determined by a continuous wave instrument at 36 °C (ref. 6), can be converted to those measured by an NMR instrument in which the effective magnetic field is parallel to the long axis of the sample, at 27 °C, by the formula: $(\delta_M)_{sc} = 2\,(\delta_M)_{cw}[(309)/(300)]$.

12 C. G. Screttas, G. A. Heropoulos, B. R. Steele and D. Bethell, *Magn. Reson. Chem.*, in the press.

13 J. Owen and J. H. M. Thornley, *Rep. Prog. Phys.*, 1966, **29**, 675.

14 See *e.g.*, E. L. Mackor, A. Hofstra and J. H. van der Waals, *Trans. Faraday Soc.*, 1958, **54**, 66.

15 J. C. Evans, C. C. Rowlands, B. J. Herold and J. M. A. Empis, *J. Chem. Soc.*, *Perkin Trans. 2*, 1984, 389.

16 A. Kuboyama, *Bull. Chem. Soc. Jpn.*, 1964, **37**, 1540.

17 W. Deuschel, *Helv. Chim. Acta*, 1951, **34**, 168; *ibid.*, 1951, **34**, 2403; F. Abel and W. Deuschel, *Chem. Ber.*, 1956, **89**, 2794.

Paper 7/08655E
Received 1*st December* 1997
Accepted 8*th July* 1998